

DFT and MP2 Molecular Orbital Determination of OH-Toluene-O₂ Isomeric Structures in the Atmospheric Oxidation of Toluene

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ABSTRACT: We have performed an exhaustive theoretical study, using a density functional theory (DFT) and *ab initio* techniques, of the possible isomers of the OH-toluene-O₂ radical. DFT calculations of the all electron type using the hybrid B3LYP approach and 6-31G* orbital basis set were employed. In addition to the well-established *ortho* position, addition of OH at C₁ on the benzene ring of toluene was also considered for the initial methylhydroxycyclohexadienyl adduct. In all, 28 different intermediate structures of the OH-toluene-O₂ system, consisting of peroxy radicals, bicyclic structures, and epoxides, have been explored through fully optimized electronic structure calculations. Starting from the 1,3-O₂-methylorthohydroxycyclohexadienyl radical, or *ortho*-OH adduct, several peroxy radicals are found to have low-lying structures contained within a small energy range (about 1 kcal/mol). Only two bicyclic structures are stable with respect to the methylhydroxycyclohexadienyl radical plus O₂, one of them being clearly favored. The four possible epoxy structures are all found to lie more than 15 kcal/mol lower than any of their peroxy and bicyclic isomers. The preference, first noted by Bartolotti and Edney, for structures in which the OH group lies on the same side of the ring as the O₂ group, is obeyed in all cases. If the 1-CH₃, 1-OH cyclohexadienyl radical (or C₁-OH adduct) is used as the initial adduct, three peroxy radicals are expected to be formed, while two bicyclic structure and three epoxides need to be considered. These structures are found to be, in general, less stable than the ones arising from the *ortho* adduct. However,

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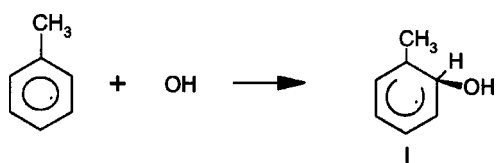
the 4-O, 2,3-epoxy, 1,1-methylhydroxycyclohexadienyl radical is found to be the most stable of all the isomers considered, and this, by more than 3 kcal/mol. In this work, most structures were also calculated with the MP2 method with a 6-31G* basis set. The geometries obtained with the two methods are similar. Contrary to the B3LYP method, MP2 always yields an extra stability to structures in which the C₁ carbon atom has sp^3 hybridization. © 2000 John Wiley & Sons, Inc. J Comput Chem 21: 716–730, 2000

Keywords: aromatic hydrocarbons; atmospheric reactions; peroxy radicals; epoxides

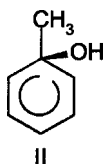
Introduction

Toluene is an important component of urban atmospheres, representing as much as 80% of all aromatic compounds, which in turn, add to more than 20% of all volatile organic compounds in the troposphere.

It is well accepted that the most important removal process for aromatic hydrocarbons in the atmosphere is the reaction with OH. The toluene–OH reaction proceeds by both H-atom abstraction and addition pathways.¹ Addition yields a methylhydroxycyclohexadienyl radical,² which possesses a relatively high stability, and which then reacts with molecular oxygen possibly producing several OH–aromatic–OO adducts. It has been well established, both experimental and theoretically, that the *ortho*-position is favored over the *meta*- and *para*-positions, regarding addition of OH to the benzene ring in toluene.³



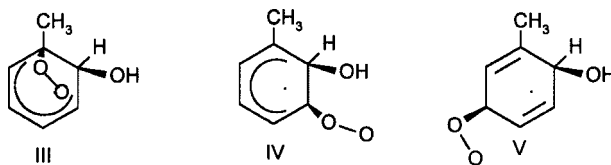
However, we have recently found⁴ that the adduct corresponding to addition at C₁:



may also be important. In fact, both Møller–Plesset and Coupled Cluster calculations set the energy of this adduct about 0.6 kcal/mol lower than the *ortho* adduct (hereforth called *o*-adduct). An analogous result has been recently reported for xylene

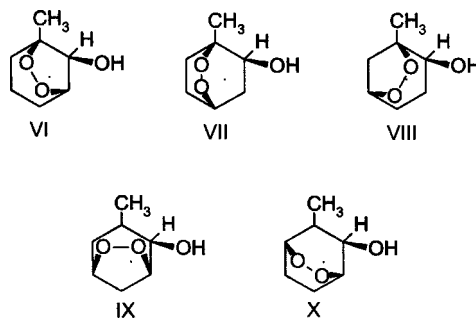
compounds.⁵ To our knowledge, for toluene, this possibility has not been considered previously.

Starting from the *o*-adduct, the following isomeric structures are possible for the subsequent addition of molecular oxygen, with the O–O group attached at positions 1, 3, or 5 on the ring:



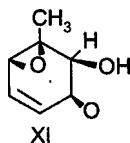
Addition to C₄ and C₆ can be ruled out because sp^3 hybridization on these carbon atoms inhibits the formation of delocalized π bonds. As argued by Atkinson and Lloyd,⁶ addition at the 5-position (structure V) should be the least thermodynamically favored, because the double bonds are nonconjugated.

According to Atkinson et al.,⁷ the next step involves the formation of bicyclic compounds with an O–O bridge across the benzene ring. Starting from any of the three peroxy radicals formed above, several isomers are possible:

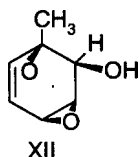


Recently, on the basis of some simple calculations using the density functional theory in a local density formalism, Bartolotti and Edney⁸ suggested that epoxide-type compounds might also be formed.

They found that the 3,6-1 structure:



was, in fact, the most stable of all the cyclic structures considered. Also, their results pointed out a significant preference for structures in which the OH group lies on the same side as the O—O group, with respect to the benzene plane, suggesting a possible interaction between the H atom on the OH group and one of the oxygen atoms on the O—O bridge. This was not discussed for the epoxide. Several other epoxides were also studied by these authors. Only one of them was found to have an energy close to that of structure XI:



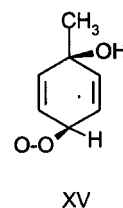
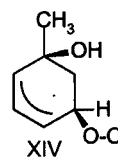
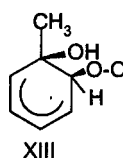
The observation by Bartolotti and Edney⁸ was confirmed experimentally by Yu and Jeffries,⁹ who carried out photo-oxidation experiments of alkylbenzene compounds under simulated atmospheric conditions and observed carbonyl products with their molecular weights matching a series of epoxide carbonyls. These authors have stressed the importance of further studies of these highly toxic and mutagenic products and their possible role in the urban atmosphere.

Andino et al.¹⁰ performed a very complete study of the whole mechanism for the photo-oxidation of toluene, the xylenes, and trimethylbenzene, using PM3 optimized geometries and single-point energies calculated with density functional theory using the hybrid B3LYP functional. They followed several channels up to the cleavage of the benzene ring and the formation of glyoxal and α -dicarbonyl compounds. These authors did not consider the possible formation of the epoxide, and all their structures had the OH group lying on the opposite side as the O—O group, with respect to the benzene ring, as originally proposed by Atkinson.

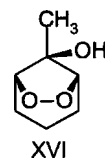
Fourteen $C_6H_5O_2$ isomers possibly involved in the mechanism of the reaction $C_6H_5 + O_2$ have been studied by Mebel and Lin¹¹ using *ab initio* molecular orbital calculations at the PUMP3/6-31G*//UHF/6-31G* + ZPE level. Some of these systems are epoxides attached to the benzene ring, analogous to those proposed in ref. 8 for toluene. From their results they were able to propose several reaction

mechanisms producing H and O atoms. The phenoxy radical had previously been the subject of calculations performed through the use of several highly accurate quantum chemistry methods.^{11, 12} The obtained results were employed to study its molecular structure and the energetics of its low-lying electronic states as well as the mechanism of its decomposition.

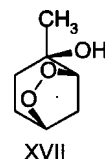
The purpose of this work, is to study theoretically, using both the density functional and the Møller-Plesset perturbative approach, the possible isomers of the OH-toluene- O_2 radical, which might be involved in the atmospheric photo-oxidation of toluene. Twenty isomers related to the *o*-adduct were considered initially. We have also studied the C_1 adduct. Its peroxy radicals were calculated, all with the OH and O_2 groups placed on the same side of the ring:



Only one bicyclic structure was studied, which allows for delocalization over three carbon atoms:

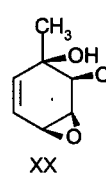
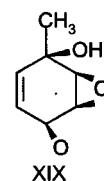
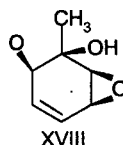


Yet, because peroxy XV was found to be the most stable one, another bicyclic structure was also investigated:



although no delocalization of the double bond is possible.

Three epoxide structures containing a ring double bond were considered:



Computational Procedure

Electronic structure calculations have been performed on 28 different intermediate structures of the adduct radical OH-toluene-O₂, possibly involved in the atmospheric reactions postulated to occur in the photo-oxidation of toluene. For some of the studied systems, several intermediate levels of theory had to be used to obtain convergence to a stable structure at a higher level of calculation. The final results in this work have been obtained with the density functional method in the generalized gradient approximation (GGA), namely the B3LYP exchange correlation potential,¹² and with the Møller-Plesset perturbation method MP2/6-31G*. The 6-31G* basis set was considered to be adequate. Introducing polarization functions on the hydrogen atoms was not deemed to be necessary, because hydrogen atoms do not play an important role in the mechanism studied here.

Fully optimized geometries were obtained with the B3LYP and MP2 methods. Zero point and thermal energy corrections to the B3LYP energies were obtained from the corresponding B3LYP vibrational frequencies calculations. For the MP2 energies, corrections were only estimated from a UHF/6-31G** frequency calculation. Because it is well known that when the energies of doublet states obtained by unrestricted methods present spin contamination, results can be improved by spin projection of the quartet component. Thus, PMP2/6-31G* energy results were used for the discussion in this work. The Møller-Plesset perturbation calculations used the frozen core approximation. All calculations were performed with the Gaussian94 package.¹³

Results

The 28 structures, corresponding to minima on the potential energy surface, have been fully optimized with the B3LYP/6-31G* density functional method. Most of the structures were also optimized with the MP2/6-31G* levels, to compare geometries and energy trends; convergence was sometimes difficult to achieve with this method.

The *o*-adduct radical is shown in Figure 1, with the numbering of the atoms.

The total B3LYP and PMP2 energies at the corresponding optimized geometries for all the systems derived from the *o*-adduct are given in Table I. Also shown are the zero point vibrational and the thermal corrections to the calculated total energy, at the

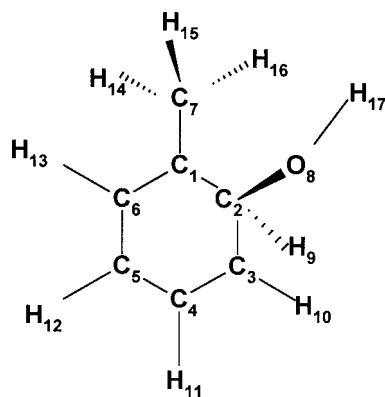


FIGURE 1. The orthomethylhydroxycyclohexadienyl radical, with the numbering of the atoms used in this work.

B3LYP and HF levels of theory. In this table the $\langle S^2 \rangle$ values before and after projection of higher spin states, for the MP2 calculations are also reported. Corresponding values for the B3LYP calculations are not given in the table, because the only $\langle S^2 \rangle$ values that differ from 0.75 before projection are obtained in the case of the 1,3-O₂ bicyclic radicals corresponding to formulae (VI_s and VI_o in the text: they are 0.778 and 0.75, before and after projection, respectively).

Structures numbered III to V are the peroxy radicals formed by direct addition of O₂ at carbons C₁, C₃, and C₅ of the ring. The letters *s* and *o* indicate whether the O—O group is on the same or on the opposite side of the ring with respect to the OH group.

Analogously, the 10 bicyclic radicals formed from these structures, with the O—O bridge lying on either side of the ring with respect to the OH group, are labeled VI_s to X_o. The epoxy radical proposed by Bartolotti and Edney⁸ is XI_s, and three other epoxy isomers derived by cleavage of the C—O—O—C bridge of the most stable bicyclic structures, VI_s and VI_o are labeled XI_o, XII_s, and XII_o.

The structures of the isomers derived from the C₁ adduct, which have been studied in this work, are numbered XIII_s to XV_s for the peroxy radicals, XVI_s and XVII_s for the bicyclic structures, and XVIII_s to XX_s for the epoxides. The B3LYP and PMP2 energies of these systems are given in Table II.

Relative energies, calculated with respect to the sum of the energies of the reactants, i.e., the corresponding adduct radical and O₂, are given in Tables III and IV. Frequencies for the B3LYP geometries were obtained with B3LYP at the same level, and corrections for thermal energies and the zero point energies have been included in the relative en-

TABLE I. **B3LYP/6-31G* and PMP2/6-31G* Total Energies (in Hartrees), Zero-Point Vibrational Corrections (ZPE), and Thermal Energies (TE) (in Hartrees), and MP2 (S^2) Values before and after Projection, for All the OH-Toluene-O₂ Systems Derived from the *Ortho*-OH Adduct.**

Radical	Number	B3LYP	TE(B3LYP) ZPE(B3LYP)	PMP2	TE(HF) ZPE(HF)	S^2 (before) $(S^2$ (after))
<i>o</i> -adduct						
	I	−347.323224	0.149653 0.141963	−346.181177	0.157627 0.150849	1.138 (0.847)
Peroxyl						
1-O ₂	III _s	−497.654769	0.160144 0.150764	−496.139526	0.169604 (0.162660)* 0.161594 (0.153463)*	0.762 (0.752) (0.752)
1-O ₂	III _o	−497.650257	0.160311 0.150584	−496.135194	0.169767 0.161666	0.761 (0.750)
3-O ₂	IV _s	−497.657650	0.160607 0.151088	−496.138669	0.170012 (0.163237)* 0.161851 (0.153791)*	0.762 (0.752)
3-O ₂	IV _o	−497.653913	0.160856 0.150988			
5-O ₂	V _s	−497.655493	0.161077 0.151493	−496.136221	0.170519 0.162274	0.780 (0.751)
5-O ₂	V _o	−497.652758	0.160762 0.150876	−496.133185	0.170278 0.161960	0.774 (0.751)
Bicyclic						
1,3-O ₂	VI _s	−497.668288	0.159956 0.151271	−496.167395	0.169097 0.161692	0.961 (0.758)
1,3-O ₂	VI _o	−497.664251	0.159964 0.151252	−496.162695	0.169188 0.161783	0.959 (0.758)
1,4-O ₂	VII _s	−497.631552	0.159309 0.150376			
1,4-O ₂	VII _o	−497.629064	0.159071 0.150024			
1,5-O ₂	VIII _s	−497.636182	0.159823 0.151196			
1,5-O ₂	VIII _o	−497.631118	0.159482 0.150577	−496.128452	0.169361 0.161992	0.768 (0.750)
3,5-O ₂	IX _s	−497.637056	0.160190 0.151536			
3,5-O ₂	IX _o	−497.631770	0.159877 0.150948	−496.12686	0.169741 0.162321	0.765 (0.750)
3,6-O ₂	X _s	−497.632928	0.160045 0.151007			
3,6-O ₂	X _o	−497.630482	0.160028 0.150970			

ergies reported in Tables III and IV. For the MP2 calculations, frequencies were only estimated from calculations at the HF level to verify that a stationary point had been found, and thus these zero-point corrections are not included in the final results. In

fact, in two cases, frequency calculations had to be performed at the MP2 level also, either because a small negative value was obtained at the HF level, or because some anomalous inversion was observed in the relative stability of the isomers. These results

TABLE I.
(Continued)

Radical	Number	B3LYP	TE(B3LYP) ZPE(B3LYP)	PMP2	TE(HF) ZPE(HF)	S ² (before) (S ² (after))
Epoxide						
3-O-6,1-epoxy	XI _s	−497.695034	0.160259 0.151347	−496.187522	0.170478 0.162770	0.776 (0.750)
3-O-6,1-epoxy	XI _o	−497.686598	0.159626 0.150328	−496.180541	0.170048 0.162220	0.777 (0.750)
1-O-3,4-epoxy	XII _s	−497.691585	0.160539 0.151698			
1-O-3,4-epoxy	XII _o	−497.681557	0.160100 0.150772			

Roman numbers refer to formulas shown in the text. The s and o letters indicate whether the O—O group is on the same side of the ring as the OH group, or on the opposite side. The values of the energy corrections indicated by an asterisk have been obtained from a frequency calculation carried out at the MP2 level.

TABLE II.
B3LYP/6-31G* and PMP2/6-31G* Total Energies (in Hartrees), Zero-Point Vibrational Corrections (ZPE), and Thermal Energies (TE) (in Hartrees), and MP2 (S²) Values before and after Projection, for the OH-Toluene-O₂ Systems Derived from the C₁-OH Adduct.

Radical	Number	B3LYP	TE(B3LYP) ZPE(B3LYP)	PMP2	TE(HF) ZPE(HF)	S ² (before) (S ² (after))
C ₁ -adduct	II	−347.320739	0.149117 0.141575	−496.181945	0.157028 0.150335	1.141 (0.848)
Peroxy						
2-O ₂	XIII _s	−497.651100	0.160162 0.150652	−496.133434	0.169461 0.161439	0.762 (0.752)
3-O ₂	XIV _s		0.150876	−496.076269	0.165807 0.157076	1.975 (1.552)
4-O ₂	XV _s	−497.653047	0.160464 0.151016	−496.136319	0.169984 0.161837	0.774 (0.751)
Bicyclic						
2,6-O ₂	XVI _s	−497.666013	0.159854 0.151236	−496.165993	0.167135 0.159883	0.965 (0.759)
2,4-O ₂	XVII _s	−497.624659	0.158747 0.150075	−496.123421	0.167984 0.160729	0.762 (0.750)
Epoxide						
6-O-2,3-epoxy	XVIII _s	−497.691892	0.159872 0.151068	−496.193333	0.169103 0.161541	0.779 (0.751)
4-O-2,3-epoxy	XIX _s	−497.689358	0.159688 0.150705	−496.184564	0.170063 0.162369	0.770 (0.750)
2-O-3,4-epoxy	XX _s	−497.686006	0.159783 0.150890	−496.177038	0.169824 0.162178	0.759 (0.750)

Roman numbers refer to formulas shown in the text. The s letters indicate that the O—O group is on the same side of the ring as the OH group.

TABLE III.
B3LYP/6-31G* and PMP2 Relative Energies (in kcal/mol) of the Isomers Corresponding to Addition of O₂ to the o-Adduct.

Type	Radical	B3LYP	PMP2
Peroxyl	1-O ₂ (III _s)	-4.49	-1.62 (-2.39)*
	1-O ₂ (III _o)	-1.56	+1.10
	3-O ₂ (IV _s)	-6.01	-1.08 (-1.49)*
	3-O ₂ (IV _o)	-3.51	
	5-O ₂ (V _s)	-4.36	+0.45
	5-O ₂ (V _o)	-2.84	+2.36
Bicyclic	1,3-O ₂ (VI _s)	-13.09	-19.11
	1,3-O ₂ (VI _o)	-10.55	-16.16
	1,4-O ₂ (VII _s)	+9.55	
	1,4-O ₂ (VII _o)	+10.96	
	1,5-O ₂ (VIII _s)	+6.97	
	1,5-O ₂ (VIII _o)	+9.93	+5.33
	3,5-O ₂ (IX _s)	+6.65	
	3,5-O ₂ (IX _o)	+9.77	+6.33
	3,6-O ₂ (X _s)	+9.15	
	3,6-O ₂ (X _o)	+10.7	
Epoxide	3-O-6,1-epoxy (XI _s)	-29.69	-31.74
	3-O-6,1-epoxy (XI _o)	-24.79	-27.36
	1-O-3,4-epoxy (XII _s)	-27.35	
	1-O-3,4-epoxy (XII _o)	-21.33	

B3LYP results include thermal energy corrections (TE) corrected at the same level. PMP2 results are uncorrected (see text). Energy differences are obtained with respect to the sum of the energies of the reactants: the o-adduct radical (E_{DFT} = -347.323224 hartrees, TE_{DFT} = 0.149653 hartrees; E_{PMP2} = -346.181177 hartrees), and O₂ (E_{DFT} = -150.320038 hartrees, TE_{DFT} = 0.005797 hartrees; E_{PMP2} = -149.955766 hartrees). The values indicated by an asterisk correspond to relative differences obtained with thermal energy corrections calculated at the MP2 level.

are also given in Tables I and II. Because relative stabilities are sought, rather than actual energy differences, and because energy results, without thermal energy corrections, follow exactly the same trends as the corrected energies, uncorrected PMP2 results should be reliable.

As expected, within each group of radicals (peroxyls, bicycles, and epoxides), the geometrical characteristics are similar. In addition, the geometries calculated with the MP2 and B3LYP methods are also very close, differences in bond lengths being about 0.006–0.01 Å and differences in bond angles, in most cases, within one degree, while the same structural trends are obeyed. In the rest of this article, B3LYP geometries will be used in the discussion, unless otherwise stated. In Figure 2, the two adducts are represented. The most stable species of each

TABLE IV.
B3LYP/6-31G* and PMP2 Relative Energies (in kcal/mol) of the Isomers Corresponding to Addition of O₂ to the C₁-Adduct.

Type	Radical	B3LYP	PMP2
Peroxyl	2-O ₂ (XIII _s)	-3.40	+2.68
	3-O ₂ (XIV _s)		+38.55
	4-O ₂ (XV _s)	-4.43	+0.87
Bicyclic	2,6-O ₂ (XVI _s)	-12.95	-17.75
	2,4-O ₂ (XVII _s)	+12.30	+8.97
Epoxide	6-O, 2,3-epoxy (XIX _s)	-29.18	-34.90
	4-O, 2,3-epoxy (XVIII _s)	-27.71	-29.40
	2-O, 3,4-epoxy (XX _s)	-25.54	-24.68

B3LYP results include thermal energy corrections (TE) corrected at the same level. PMP2 results are uncorrected (see text). Energy differences are obtained with respect to the sum of the energies of the reactants: the C₁-adduct radical (E_{DFT} = -347.320739 hartrees, TE_{DFT} = 0.149117 hartrees; E_{PMP2} = -346.181945 hartrees), and O₂ (E_{DFT} = -150.320038 hartrees, TE_{DFT} = 0.006142 hartrees; E_{PMP2} = -149.955766 hartrees).

group, corresponding to structures III_s, VI_s, and XI_s, for those arising from the o-adduct, and XV_s, XVI_s, and XVIII_s for those arising from the C₁-adduct are represented in Figures 3, 4, and 5. Some of their geometric parameters, calculated with B3LYP and MP2, are indicated on these figures. Charges and spin densities are given in Table V. Vibrational frequencies are also discussed.

All the optimized structures are available from the authors.

Discussion

The lowest energy structures are the epoxides. The bicyclic and peroxyl radicals are located as higher lying energy states. We will proceed to the discussion of the main features of each type of systems.

As expected, the O—O distances are longest in the bicyclic structures. On going from a peroxyl radical to a bicyclic structure the length of the O—O bond characteristically increases from 1.32 to 1.50 Å, while the corresponding C—O bond, on the contrary, decreases from 1.52 to 1.46 Å. In the epoxy radicals, the C—O bonds are even shorter, around 1.40 Å.

Overall, the Mulliken population analyses indicate an acid behavior of the H atom of the OH

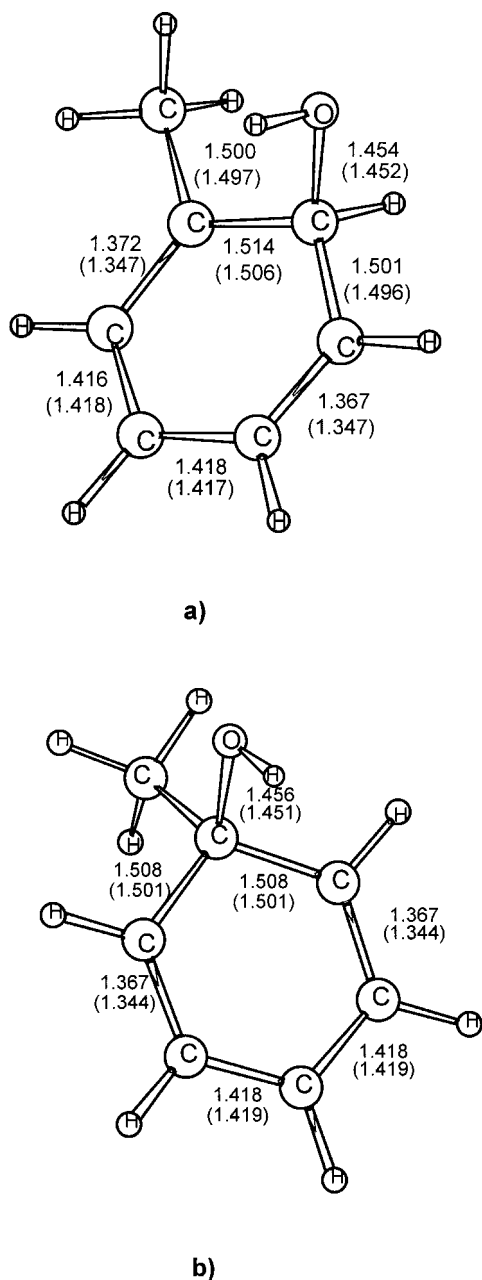


FIGURE 2. Structure and B3LYP geometric parameters of the OH-adducts: (a) isomer I, and (b) isomer II. The corresponding MP2 parameters are given in parentheses.

group. The positive charge on this H atom is typically about 0.4 compared to 0.1 for any of the other hydrogen atoms of the molecules (Table V). For peroxy radicals, Boyd et al.¹⁴ pointed out that HF densities characteristically place an accumulation of negative charge on the internal oxygen atom, while the spin density is almost entirely located on the terminal oxygen. On the contrary, Mulliken popula-

tion analyses performed using either the MP2 or the B3LYP densities, yield rather small charges on the oxygens of the O—O group, and, moreover, these are evenly distributed between these two oxygen atoms. Negative charge accumulates mainly on the oxygen atom of the OH group and on the carbon atom of the methyl group. This is true for all the type of systems considered in this work.

Regarding the spin densities, in all cases, spin densities are about 0.3 on the internal and 0.7 on the terminal oxygen atoms. The spin densities on the carbon atoms depend on the position of the unpaired electron in each system.

PEROXYL RADICALS

Three sites of attack for the O₂ molecule on the *ortho*-methylhydroxy hexadienyl radical have been considered. According to Atkinson et al.,² and on the basis of Benson's thermochemical rules,¹⁵ the most stable peroxy radical should be the III isomer. On the other hand, Andino et al.¹⁰ predict, on the basis of B3LYP//PM3 calculations, that the IV isomer should be favored. Both of these authors, however, only considered the possibility of O₂ adding to the opposite side of the ring from OH.

In the present work it was found that, more important energetically than the site of addition to the ring, it is the side of the ring on which the O₂ molecule attacks which matters most. In all cases, a clear preference is observed when the addition occurs on the same side of the ring that contains the OH substituent. This type of structure allows for an interaction between the terminal oxygen (O₁₉) and the hydrogen of the OH group (H₁₇), which stabilizes the peroxy radicals by between 1.5 and 3.0 kcal/mol, depending on the position of the O₂ addition. The distance between these atoms is 1.90 Å in the most stable DFT structure IV_s (Fig. 3). The OH and O—O groups rotate so as to minimize the O₁₉...H₁₇ distance, which is 2.32 Å in the V_s isomer. The above stabilization is observed with any of the two methods of calculation employed in this work.

According to the B3LYP calculations, the peroxy radical with the O—O group attached at C₃ (structure IV_s) is the most stable one. The other two peroxy radicals having all oxygen atoms on the same side of the ring have energies that are less than 1.5 kcal/mol above the lowest one, and thus, one may expect that, at room temperature, all of them should be formed. For peroxy radicals having OH and O₂ on opposite sides, our results are in agreement with those reported by Andino et al.¹⁰

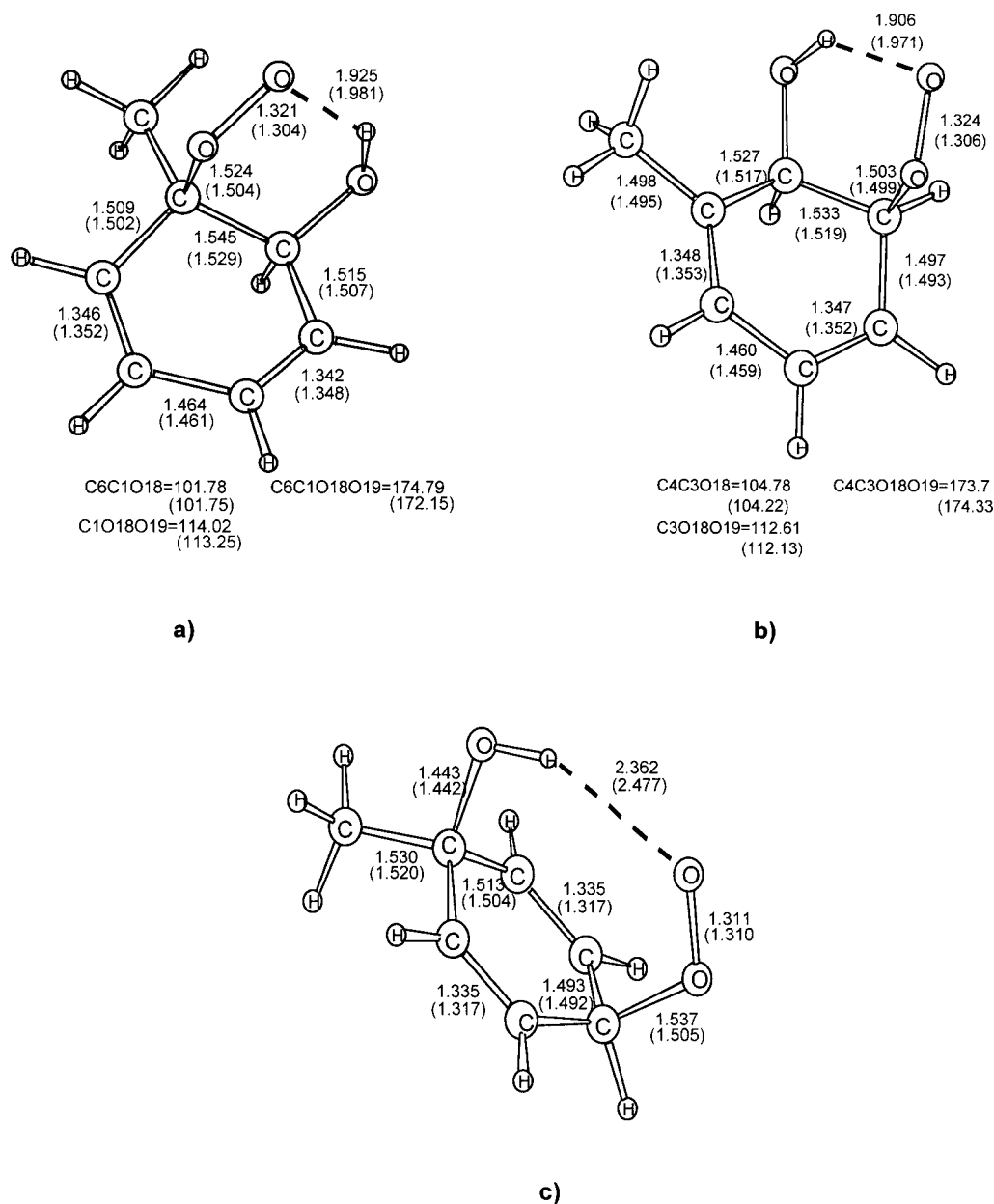


FIGURE 3. Structure and B3LYP geometric parameters of two peroxyl radicals arising from the ortho adduct: (a) isomer III_s , and (b) isomer XV_s , and one derived from the ipso adduct; (c) isomer XV_s . The corresponding MP2 parameters are given in parentheses.

A discrepancy is observed between the most stable peroxyl radicals as determined from the MP2 calculations and those obtained with B3LYP: MP2 favors addition of O_2 at C_1 on the *o*-adduct. In fact, we have noted, in several cases,⁵ that the MP2 method consistently emphasizes the positive interactions in compounds where addition occurs on the substituted carbon atom on the ring. In the case of the *o*-adduct of toluene, in the MP2 most favorable structure, the III_s , the $\text{O}-\text{O}$ group points towards

the ring, while the optimum geometry of this structure as optimized with B3LYP, has the $\text{O}-\text{O}$ group sticking away from the ring, allowing for interaction with OH . Although both methods agree on the existence of two minima differing on the orientation of the $\text{O}-\text{O}$ group, their relative energies are inverted. The difference between the energies of isomers III_s and IV_s with MP2, however, is only 0.5 kcal/mol.

Considering the peroxyl radicals obtained from the C_1 -adduct, both methods agree on their relative

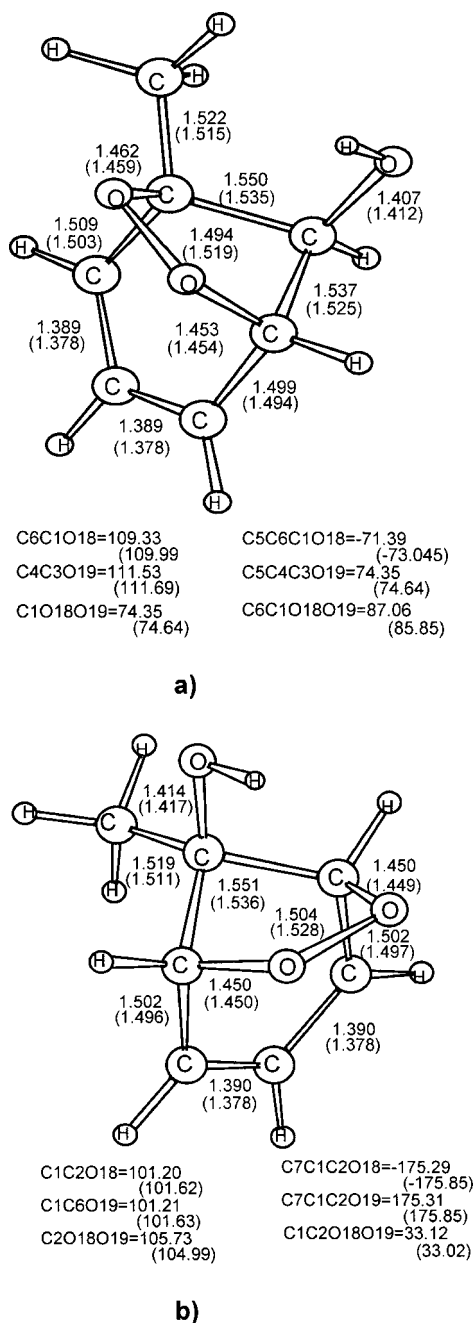


FIGURE 4. Structure and B3LYP geometric parameters of two bicyclic compounds: (a) isomer VI_s, and (b) isomer XVI_s. The corresponding MP2 parameters are given in parentheses.

stabilities. Addition of O₂ at C₃ is extremely unfavorable, its energy being almost 40 kcal/mol higher than that of the other two isomers. In fact, with the B3LYP method, it was not possible to find a stationary energy for this system. Such a high relative energy is in line with the existence, in this structure,

of only one double bond delocalized over three carbon atoms (compared with the reactants), while in the other two peroxy radicals two double bonds may be formed. The fact that addition at C₄ yields a peroxy radical that is more stable than the one arising from addition at C₂, however, is more surprising, because the former presents two localized double bonds, while the latter has two delocalized double bonds. The difference in the energies of these two isomers, as obtained with both methods, is, however, more than 1 kcal/mol.

When the B3LYP results of both sets of peroxy radicals are compared, it is clear that, globally, structure IV_s is the most stable one, while structures III_s and V_s have very similar energies, about 1.5 kcal/mol higher. The peroxy radicals derived from the C₁-adduct are all less stable.

With MP2, structures III_s and IV_s are favored, while V_s and XV_s lie almost 2 kcal/mol higher in energy. When the C₁ position is already occupied, which is the case in the C₁-adduct, then B3LYP and MP2 agree on the next position to be occupied. In Table VI, the energies of all the peroxy radicals, calculated by the two methods, have been grouped, relative to the sum of the energies of toluene, OH, and O₂.

It is worth noting that, while with B3LYP all the reaction energies of the peroxy radicals turn out to be negative, only the four most stable ones may be expected to have negative reaction energies with the MP2 method (if thermal corrections are included at the same level).

To try to find out which is the overall most stable peroxy radical, and at the same time, to validate the positive interactions observed in the MP2 geometries when the C₁ carbon is substituted, calculations with the Coupled Cluster method have been performed using the 6-31G** basis set, at the best MP2 and B3LYP geometries of the III_s and IV_s structures. The results are given in Table VII. With any set of geometries, CC definitely favors addition at C₁. It is also clear that MP2 geometries yield lower CC energies than B3LYP geometries (this has also been observed for toluene adducts⁴).

To evaluate a possible bias due to the basis set superposition error, MP2 single-point calculations were also performed on structures III_s and IV_s, using a correlation consistent triple seta basis set (Table VIII). Again, structure III_s was the favored one.

The possibility that the basis set superposition error could be, at least, partially responsible for the much higher stability of the same side O₂-OH adducts (where O...H interactions are sometimes observed) with respect to the opposite side adducts

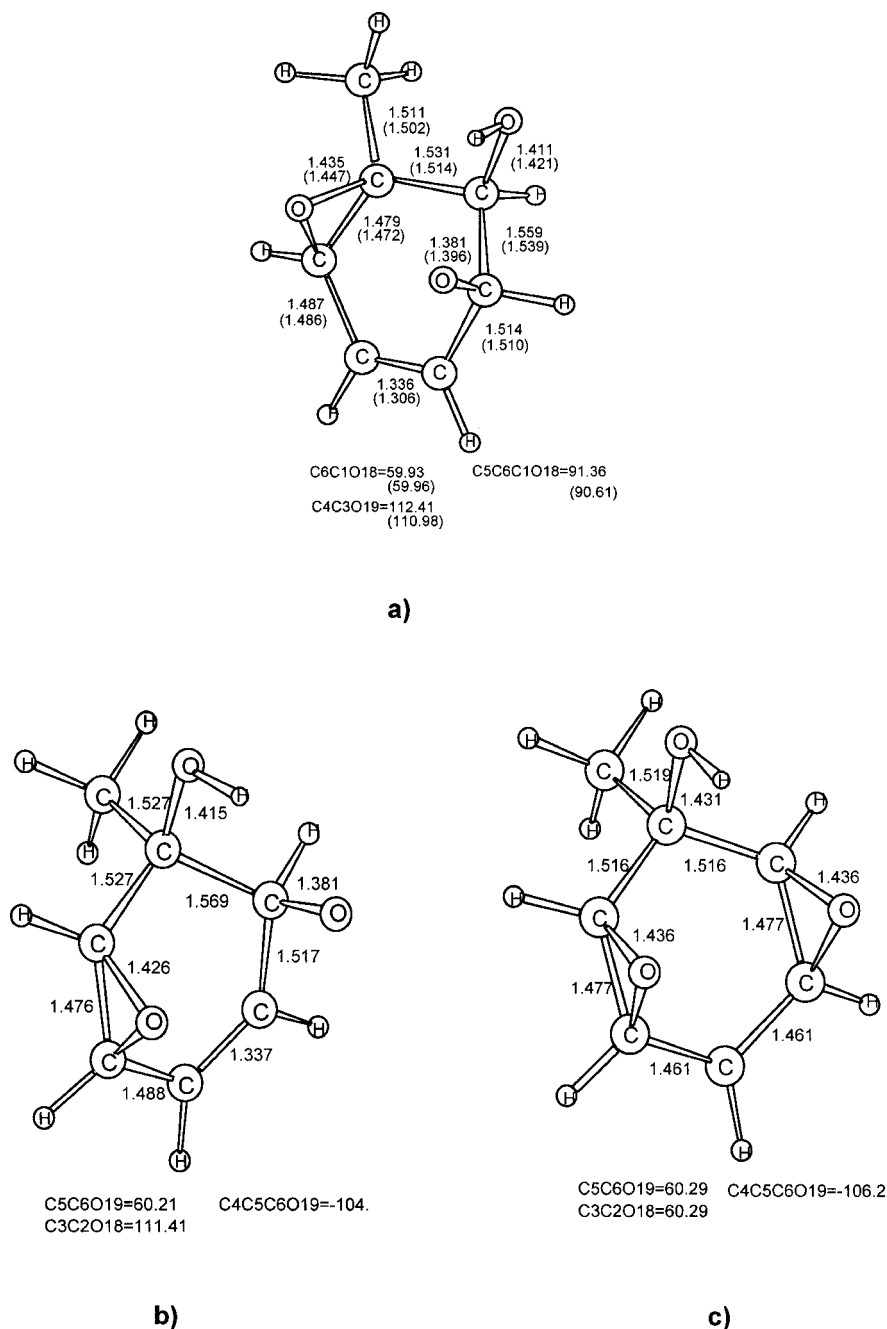


FIGURE 5. Structure and B3LYP geometric parameters of epoxide structures: (a) isomer XI_s, (b) B3LYP geometry for isomer XVIII_s, and (c) MP2 geometry for isomer XVIII_s.

was suggested by an anonymous referee. Indeed, the difference between the III_s and III_o peroxy radicals, as obtained with the 6-31G*, is 0.5 kcal/mol larger than the cc-pVTZ.

In alkylperoxy radicals, Lightfoot et al.¹⁶ indicated that the O—O stretching frequency was about 1100 cm⁻¹ and remained almost unchanged over a series of compounds, whereas the C—O stretching

frequency showed considerable variation (between 700 and 900 cm⁻¹), decreasing from primary, to secondary, to tertiary radicals. Our B3LYP frequencies (unscaled) are found around 800 cm⁻¹ for C—O and at about 1190 cm⁻¹ for O—O. In the peroxy radicals with the O—H and O—O groups on the same side of the ring, an O...H bridge presents a frequency at 320 cm⁻¹.

TABLE V. Charges and Spin Densities Calculated with the MP2 and B3LYP Methods for Characteristic Structures in Each Group.

Radical	Atom	Charge MP2	Charge B3LYP	Spin Density MP2	Spin Density B3LYP
<i>o</i> -adduct	C ₁	0.07	0.13	0.30	0.42
	C ₂	0.03	0.03	−0.01	−0.05
	C ₃	−0.19	−0.16	0.34	0.43
	C ₄	−0.15	−0.10	−0.15	−0.21
	C ₅	−0.19	−0.15	0.63	0.56
	C ₆	−0.20	−0.16	−0.13	−0.22
	C ₇	−0.53	−0.51	−0.01	−0.03
	O ₈	−0.65	−0.61	0.04	0.05
	H ₁₇	0.41	0.38	0.01	0.01
1-O ₂ (III _s)	C ₁	0.18	0.19	0.02	−0.02
	C ₂	0.08	0.11	−0.03	0.01
	C ₃	−0.19	−0.14	0.05	0.00
	C ₄	−0.16	−0.11	−0.11	0.00
	C ₅	−0.14	−0.11	0.12	0.00
	C ₆	−0.18	−0.14	−0.05	0.00
	C ₇	−0.52	−0.46	0.00	0.00
	O ₈	−0.69	−0.65	0.00	0.00
	H ₁₇	0.45	0.42	0.00	0.00
	O ₁₈	−0.22	−0.16	0.31	0.34
1,3-O ₂ (VI _s)	O ₁₉	−0.15	−0.19	0.69	0.65
	C ₁	0.15	0.22	−0.04	−0.04
	C ₂	0.11	0.12	0.02	0.02
	C ₃	−0.02	−0.02	−0.04	−0.04
	C ₄	−0.14	−0.10	0.67	0.64
	C ₅	−0.16	−0.12	−0.27	−0.26
	C ₆	−0.13	−0.10	0.67	0.064
	C ₇	−0.50	−0.47	0.00	0.00
	O ₈	−0.67	−0.62	0.00	0.00
	H ₁₇	0.44	0.41	0.00	0.00
3-O-6,1-epoxy (XI _s)	O ₁₈	−0.30	−0.30	0.05	0.04
	O ₁₉	−0.30	−0.29	0.00	0.04
	C ₁	0.21	0.27	0.10	0.00
	C ₂	0.11	0.11	−0.01	0.02
	C ₃	0.01	0.04	0.12	−0.04
	C ₄	−0.17	−0.13	−1.88	−0.02
	C ₅	−0.12	−0.07	+1.88	0.00
	C ₆	−0.02	0.00	−0.34	0.00
	C ₇	−0.51	−0.47	0.00	0.00
	O ₈	−0.67	−0.63	0.00	0.01
	H ₁₇	0.44	0.41	0.00	0.00
	O ₁₈	−0.47	−0.46	0.15	0.03
	O ₁₉	−0.30	−0.32	0.92	0.86

BICYCLIC RADICALS

Except for the 1,3-O—O bridged structure, with the bridge on either side of the benzene ring, the

formation of all the other bicyclic radicals originating from the *o*-OH adduct is an exothermic process. Structures VI_s and VI_o are about 20 kcal/mol more stable than any of the others. Additionally, the

TABLE VI.
B3LYP/6-31G* and PMP2/6-31G* Relative Energies
(in kcal/mol) of the Most Stable Peroxyl Radicals
Calculated with Respect to the Sum of the Energies
of the Reactants.

Adduct	Peroxyl	B3LYP	PMP2	Ref. 8
o-adduct		-20.78	-18.93	
	III _s	-28.00	-20.55	-21.974
	IV _s	-29.81	-20.01	-22.682
	V _s	-28.46	-18.48	-19.065
C ₁ -adduct		-19.22	-19.41	
	XIII _s	-25.70	-16.73	
	XV _s	-26.92	-18.54	

Toluene (E(B3LYP) = -271.566648 hartrees, E(PMP2) = -270.62844 hartrees), OH (E(B3LYP) = -75.723454 hartrees, E(PMP2) = -75.522571 hartrees) and O₂ (E(B3LYP) = -150.320038 hartrees, E(PMP2) = -149.955766 hartrees). The DFT values of ref. 8 are also given for comparison.

VI_s isomer is more than 2.5 kcal/mol more stable than VI_o. The B3LYP and MP2 results agree on these points. The particular stability of isomer VI_s is easily explained because it is the only one that possesses a delocalized allyl- π -type system, all other structures having only one localized double bond.

In fact, both bicycles VI_s and VI_o are also, characteristically, the only ones presenting considerable spin contamination, not only with MP2, but also with B3LYP calculations. The spin density was found to be delocalized on the carbon atoms of the allyl bond, and so one may expect some contribution from a quartet state with three unpaired π electrons.

The VI_s isomer is directly obtainable from either of the peroxy radicals III_s and IV_s, which are the most stable according to PMP2 and B3LYP, respectively.

If the attack by O₂ occurs on the opposite side of the ring with respect to the OH group, an analogous result is obtained. Only one position for the O—O

TABLE VII.
Single-Point CCD/6-31G Total Energy Results (in**
Hartrees) for Peroxyl Radicals III_s and IV_s, Calculated
at the MP2 and B3LYP Optimum Geometries.

System	CCD//B3LYP	CCD//MP2
III _s	-496.264853	-496.265562
IV _s	-496.264168	-496.264857

TABLE VIII.
Single-Point MP2 Total Energy Results (in Hartrees)
for Selected Peroxyl Radicals, Calculated at the MP2
Optimum Geometries Using the cc-pVTZ Basis Set.

System	MP2/cc-pVTZ
III _s	-496.730633
IV _s	-496.730284
III _o	-496.727129

bridge yields a stable structure (the 1,3-O—O isomer, VI_o), which corresponds to the cyclization of any of the two most stable peroxy radicals, III_o and IV_o.

For the bicyclic radicals formed from the bridging of the O—O group in the peroxy radicals of the C₁-OH adduct, the only stable structure is the 2,6-O—O (XVI_s). By analogy with the other bicyclic structures studied in this work, we expect the XVI_o isomer to be also stable, though a few kilocalories less stable than XVI_s. Isomer XVI_s presents a delocalized allyl-type double bond with three electrons on it, and the calculations show a significant contribution from a quartet state, which is, however, projected out in the PMP2 energy result.

It is interesting to note that the XVI_s isomer cannot be obtained directly by cyclization of the most stable peroxy radical XV_s, which is the one with the O—O group attached to C₄. Yet, because both B3LYP and MP2 results predict that the XIII_s peroxy radical, with O—O attached at C₁ is less than 2 kcal/mol less stable, it is conceivable that, at room temperature, structure XVI_s could be formed.

Comparing the energies of both sets of bicyclic structures, it can be seen that, overall, two isomers are especially stable: VI_s and XVI_s, the former one being slightly favored. Thus, it is possible that both of these isomers could be intermediates in the photo-oxidation of toluene.

No experimental frequencies are available for this type of structure. For the most stable one VI_s, a vibration involving the C—O—O—C bridge is found at 825 cm⁻¹ (unscaled), and two vibrations of either one or the other of the C—O bonds appear at 1006 cm⁻¹ and 1106 cm⁻¹. When these values are compared to the O—O and C—O frequencies in peroxy radicals, it is noticed that their values are reversed, reflecting the weakening of the O—O bond and the strengthening of the C—O bond when the terminal oxygen of a peroxy radical attaches to a carbon atom of the ring.

EPOXY RADICALS

Seven epoxide structures were geometry optimized. All of them are remarkably stable isomers, when compared to either the peroxy radicals or the bicyclic structures, having energies that are as much as 30 kcal/mol lower than the former and about 12 kcal/mol lower than the latter.

For the isomers derived from the *o*-OH adduct, the possibility of the epoxide group being on either side of the benzene ring with respect to the OH group was considered. Results show a preference for all oxygen atoms on the same side, even more pronounced than for peroxy radicals and bicyclic structures. Epoxide XI_s is more probable. This isomer can be expected to be formed directly by a rearrangement of the bicyclic radical VI_s.

Two of the isomers derived from the C₁-OH adduct have very low energies. In fact, according to the PMP2 result, the epoxide radical XIX_s is especially stable, its energy being about 3 kcal/mol lower than any of the others. This is not the case with B3LYP. The difference is easily explained if one looks at the optimized geometries obtained with the two methods (Fig. 5b and 5c). The MP2 structure is a very symmetric structure, presenting two identical epoxy groups, with no double bond and with the unpaired electron localized on C₄. Instead, the B3LYP geometry has only one epoxy group, a double bond between C₃ and C₄, and its spin density is localized on the lone oxygen atom. The latter is bent in the direction of C₃, but at a distance of 2.39 Å. Attempts to transform one geometry into the other failed to provide minima.

It is interesting to point out that, for structures in which the OH and the O—O groups lie on opposite sides of the ring, it is observed that, while for the bicyclic structures H₁₉ always points towards the ring, in the epoxides this hydrogen atom points outwards.

Two calculated coupled stretching vibrations of the bridged C—O—C bonds in the epoxide radicals take place at about 800 and 900 cm⁻¹, in agreement with the results obtained by Mebel and Lin¹¹ for C₆H₅=(O)_{br} radicals containing an epoxide group and a C=O double bond. The C—O single bond in structure XI_s is found at 1252 cm⁻¹, slightly higher than in the bicyclic structures.

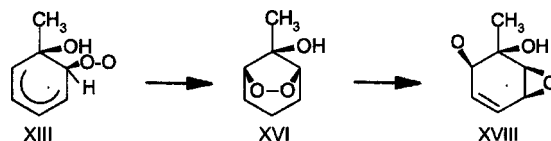
Conclusions

In this work, OH-toluene-O₂ isomeric structures corresponding to the OH addition at the C₁ position of the ring have been considered for the first time.

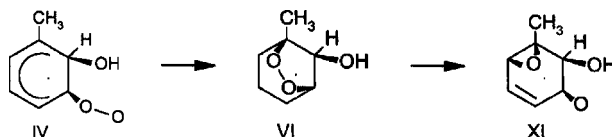
Two distinct sets of isomers were considered for the methylhydroxycyclohexadienyl radical + O₂ addition reaction, according to the side of the benzene ring on which the O₂ molecule attack occurs. Radicals with the oxygen atoms on the same side of the ring were systematically found to be more stable than the others. Structures on both sides may occur, however, but it is obvious that migration from one to another is impossible.

In agreement with the work by Bartolotti and Edney,⁸ the most stable radicals are found to be the epoxides, which have energies more than 10 kcal/mol lower than those of the few stable bicyclic structures (the latter must have the possibility of forming an allyl type π bond in the ring). The least stable radicals are the peroxy radicals: their energies are about 10 kcal/mol less than the bicyclic radicals, and in fact, their reaction energies are only a few kcal/mol. The results obtained with the MP2 method indicate that only two of them are formed in an exothermic reaction. The B3LYP method, instead, yields small negative reaction energies for all the peroxy radicals. However, the sign of the energy difference in B3LYP has to be used with caution when the numbers are small, because it is well known that this method has been shown to give negative reaction energies in cases in which it is certain that they should be positive, for example, energy barriers in hydrogen abstraction reactions from alkanes.¹⁷

Two epoxides structures show a high stability: they are XI_s and XVIII_s. Their B3LYP energies are very similar, but the MP2 method favors the latter by as much as 3.3 kcal/mol. Structure XVIII_s cannot be formed directly from the reactants. A conceivable mechanism for its formation in the troposphere could involve the following sequence of intermediates:



However, peroxy XIII_s is not particularly stable. In fact, its energy is almost 3 kcal/mol above several of the others, the latter corresponding, in general, to the addition of O₂ to the *o*-adduct. Thus, another pathway may be energetically more favorable, which leads to epoxide XI_s:



Although with the two methods employed in this work, the absolute values of the energy differences do not agree, the observed trends are very similar, which is particularly meaningful because these methods are based on quite different approaches. Unfortunately, no experimental data for the intermediate radicals are available for comparison. Yu and Jeffries,⁹ however, have found evidence of the formation of epoxide intermediates in mass spectra. The present numerical results may provide a sound theoretical basis for the elucidation of the mechanism of aromatic hydrocarbon photo-oxidation in the troposphere.

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